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(54) Title: HIGH TEMPERATURE ALLOYS

(57) Abstract: An improved nickel-chromium-iron alloy is provided, which comprises up to about 5 % of hafnium-containing particles. In one embodiment, an improved creep resistant castable oxide dispersion strengthened nickel-chromium-iron alloy comprises up to about 5 % of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles. Further embodiments of the improved alloy can comprise additionally up to about 15 % by weight aluminium. The alloy is particularly useful in the production of creep resistant tubes and castings, for example, for the petrochemical market.

AMENDED CLAIMS

[Received by the International Bureau on 09 August 2004 (09.08.2004); original claims 15-17, 22, 25, 44, 46-47, 50, 58-59 cancelled' original claims 37 and 38 replaced by amended claims 37 and 38 (14 pages)]

1. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

Carbon	0.01 – 0.7%
Silicon	0.1 – 3.0%
Manganese	0 – 2.5%
Nickel	15 – 90%
Chromium	5 – 40%
Molybdenum	0 – 3.0%
Niobium	0 – 2.0%
Tantalum	0 – 2.0%
Titanium	0 – 2.0%
Zirconium	0 – 2.0%
Cobalt	0 – 2.0%
Tungsten	0 – 4.0%
Hafnium	0.01 – 4.5%
Aluminium	0 – 15%
Nitrogen	0.001 – 0.5%
Oxygen	0.001 – 0.7%

balance iron and incidental impurities,

with the proviso, that at least one carbide forming element whose carbide is more stable than chromium carbide selected from niobium, titanium, tungsten, tantalum and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

2. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

Carbon	0.01 to 0.5%

Silicon	0.01 to 2.5%
Manganese	0 to 2.5%
Nickel	15 to 50%
Chromium	20 to 40%
Molybdenum	0 to 1.0%
Niobium	0 to 1.7%
Titanium	0 to 0.5%
Zirconium	0 to 0.5%
Cobalt	0 to 2.0%
Tungsten	0 to 1.0%
Hafnium	0.01 to 4.5%,

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

3. An alloy according to claim 1 having the following composition, by weight:

Carbon 0.3 to 0.7%	
Silicon	0.1 to 2.5%
Manganese	2.5% max.
Nickel	30 to 40%
Chromium	20 to 30%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.0% max.
Tungsten	1.0% max.

Nitrogen	0.001 – 0.5%
Oxygen	0.001 – 0.7%

Balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

4. An alloy according to claim 1 having the following composition, by weight:

Carbon	0.03 to 0.2%
Silicon	0.1 to 0.25%
Manganese	2.5% max.
Nickel	30 to 40%
Chromium	20 to 30%
Molybdenum	3.0% max.
Niobium	1.7% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.05% max.
Tungsten	1.0% max.
Aluminium	0 – 15.0%
Nitrogen	0.001 – 0.5%
Oxygen	0.001 – 0.7%

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

5. An alloy according to claim 1 having the following composition, by

weight:

Carbon	0.3 to 0.7%
Silicon	0.01 to 2.5%
Manganese	2.5% max.
Nickel	40 to 60%
Chromium	30 to 40%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	1.0% max.
Zirconium	1.0% max.
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 – 15.0%
Nitrogen	0.001 – 0.5%
Oxygen	0.001 – 0.7%

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

6. An alloy according to claim 1 having the following composition, by weight:

Carbon	0.03 to 0.2%
Silicon	0.1 to 2.5%
Manganese	2.5% max.
Nickel	40 to 50%
Chromium	30 to 40%
Molybdenum	3.0% max.
Niobium	2.0% max.

Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 – 15.0%
Nitrogen	0.001 – 0.5%
Oxygen	0.001 – 0.7%

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

7. An alloy according to claim 1 having the following composition, by weight:

Carbon	0.3 to 0.7%
Silicon	0.01 to 2.5%
Manganese	2.5% max.
Nickel	19 to 22%
Chromium	24 to 27%
Molybdenum	3.0% max.
Niobium	2.0% max
Hafnium	0.01 to 4.5%
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 – 15.0%
Nitrogen	0.001 – 0.5%
Oxygen	0.001 – 0.7%

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is

present and that at least part of the hafnium is present as finely divided oxide particles.

8. An alloy according to claim 1 having the following composition, by weight:

Carbon	0.03 to 0.2%
Silicon	0.1 to 2.5%
Manganese	2.5% max
Nickel	30 to 45%
Chromium	19 to 22%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.0% max.
Tungsten	1.0% max.
Aluminium	0 – 15.0%
Nitrogen	0.001 – 0.5%
Oxygen	0.001 – 0.7%

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

9. An alloy according to any one of claims 1, 2, 3, 5, or 7, having a carbon content of from 0.3 to 0.5% by weight.

10. An alloy according to claim 1 or 2, having a carbon content of from 0.03 to 0.2% by weight.

11. An alloy according to claim 1, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.01 to 3.0%.

12. An alloy according to claim 11, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.

13. An alloy according to claim 11 or 12, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.2 to 0.5%.

14. An alloy according to any one of the preceding claims, in which the amount of carbon in the alloy, by weight, is from 0.03 to 0.2% and the amount of hafnium in the alloy, by weight, is from 1 to 4.5%.

18. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less.

19. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 5 microns to 0.25 microns, or less.

20. An alloy having any one of the following compositions, by weight:

Carbon	0.45%
Silicon	1.3%
Manganese	0.9%
Nickel	33.8%
Chromium	25.7%
Molybdenum	0.03%
Niobium	0.85%

Hafnium	0.25%
Titanium	0.1%
Zirconium	0.01%
Cobalt	0.04%
Tungsten	0.01%
Nitrogen	0.1%
Iron	balance,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

Carbon	0.07%
Silicon	1.0%
Manganese	0.98%
Nickel	32.5%
Chromium	25.8%
Molybdenum	0.20%
Niobium	0.04%
Hafnium	1.1%
Titanium	0.12%
Zirconium	0.01%
Cobalt	0.04%
Tungsten	0.08%
Nitrogen	0.1%
Iron	balance,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

Carbon	*0.34%*

Silicon	*1.68%*
Manganese	*1.10%*
Nickel	*32.0%*
Chromium	*21.3%*
Molybdenum	*0.01%*
Niobium	*0.80%*
Hafnium	*0.25%*
Titanium	*0.12%*
Zirconium	*0.01%*
Aluminium	*3.28%*
Cobalt	*0.04%*
Tungsten	*0.01%*
Iron	*balance,*

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

Carbon	*0.42%*
Silicon	*1.79%*
Manganese	*1.17%*
Nickel	*33.2%*
Chromium	*23.3%*
Molybdenum	*0.02%*
Niobium	*0.77%*
Hafnium	*0.24%*
Titanium	*0.10%*
Zirconium	*0.01%*
Aluminium	*1.64%*
Cobalt	*0.04%*
Tungsten	*0.08%*
Iron	*balance,*

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

21. An alloy according to any one of the preceding claims substantially as described in Examples 1 to 4.

23. A nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.

24. An oxide dispersion strengthened nickel-chromium-iron alloy which comprises up to about 5% by weight of hafnium, with at least part of the hafnium being present as finely divided oxidised particles.

26. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.

27. A method according to claim 26, in which the alloy is an alloy as claimed in any of claims 1 to 25.

28. A method according to claim 26 or 27, wherein the hafnium particles have a particle size of less than 50 microns.

29. A method according to any one of claims 26 to 28, in which the amount of hafnium added to the melt is from 0.01 to 3.0% by weight.

30. A method according to any one of claims 26 to 29, wherein the hafnium particles are added to the melt shortly before pouring the molten alloy into a mould.

31. A method according to claim 30, in which the hafnium particles are

added to the molten alloy in a ladle.

32. A method according to claim 30, in which the hafnium particles are added to the molten alloy in the furnace

33. A method according to anyone of claims 26 to 32, in which the hafnium is electrolytic hafnium.

34. A method according to any one of claims 26 to 33, wherein the level of oxygen in the melt is varied by the addition of one or more substance selected from the group:

silicon,
chromium,
manganese,
calcium,
CaSi,
CaSiMn,
niobium,
titanium,
zirconium.

35. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and varying the level of oxygen in the melt by, the addition of at least one substance chosen from the group:

silicon,
chromium,
manganese,
calcium,
CaSi,
CaSiMn,
niobium,
titanium,

zirconium.

36. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that the formation of detrimental oxide from the reactive elements titanium, zirconium, aluminium is reduced.

37. A method according to any one of claims 26 to 36 wherein any one of the elements titanium or zirconium are added after hafnium into the melt.

38. A method as claimed in claim 37 wherein any one of the elements titanium or zirconium are added after the hafnium in the melt, and just before pouring in the mould.

39. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and which controls the partial pressure of oxygen to permit the oxidation of the hafnium in situ.

40. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and which controls the free oxygen content to permit the oxidation of the hafnium in situ.

41. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and which controls the partial pressure of at least one element selected from the following group:

oxygen,
carbon,
nitrogen,

hydrogen;

to permit the oxidation of the hafnium in situ.

42. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy and which permits the oxidation in situ of beneficial oxide dispersion as hafnium oxide, avoiding the formation of detrimental precipitates.

43. A method as claimed in claim 42 which limits in situ oxidation to beneficial oxide dispersion of hafnium oxides and avoid its reaction with slag.

45. A method according to any of claims 26 to 44, in which the melt temperature is in the range of from 1350°C to 1700°C.

48. A method according to any one of claims 26 to 47, in which the alloy is formed into a tube by rotational moulding.

49. A method according to any one of claims 26 to 48 substantially as described in Examples 1 to 4.

51. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium particles to the melt before pouring.

52. A creep resistant alloy tube formed from a nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.

53. A tube according to claim 52, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.

54. A nickel-chromium-iron alloy tube comprising up to about 5% of

hafnium-containing particles substantially as herein before described.

55. A tube formed from an alloy according to any of claims 1 to 25 by rotational moulding.

56. A nickel-chromium-iron alloy having a structure and composition substantially as described and illustrated in any one of Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.

57. A nickel-chromium-iron alloy having a structure substantially as described and illustrated in Figures 5 or 6 of the accompanying Drawings.

60. A tube formed from an alloy according to any of claims 1 to 25 by rotational moulding.

61. An alloy according to any one of claims 1 to 25, 56 and 57 produced by a method according to any one of claims 26 to 51.